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Skutterudites: An Update

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Abstract

Materials with the skutterudite crystal structure possess attractive transport properties and have a good potential for achieving ZT values substantially larger than for state-of-the-art thermoelectric materials. Studies conducted at JPL on $CoAs_3$, $RhAs_3$, $CoSb_3$, $RhSb_3$ and $IrSb_3$ have shown that p-type conductivity samples are characterized by carriers with low effective masses and very high nobilities, low electrical resistivities and moderate Seebeck coefficients. The carrier nobilities of n-type samples are about an order of magnitude lower, but low electrical resistivities and relatively large Seebeck coefficients can still be obtained at high doping levels. The room temperature lattice thermal conductivities of these binary skutterudites was found to be 7 to 10 times larger than that of Bi_2Te_3. This results in low ZT values at 300K, though very heavily doped n-type $CoSb_3$ samples can achieve ZT~1 at 600°C. Several research groups, mostly in the U. S., are now working on understanding and optimizing the transport properties of skutterudites. Most of the efforts are focusing on reducing the lattice thermal conductivity by filling the empty octant cages in the skutterudite structure with rare earth atoms. Additional approaches have also been pursued at JPL, in particular the formation of solid solutions and alloys, and the study of novel ternary skutterudite compounds. Recent experiments have demonstrated that ternary compounds such as $Ru_{0.5}Pd_{0.5}Sb_3$ and filled skutterudites such as $CeFe_4Sb_{12}$ had much lower lattice thermal conductivity. High ZT values have been obtained for several filled skutterudites in the 500-700°C temperature range, but figures of merit at 300K are still low. This paper reviews recent experimental and theoretical results on skutterudites with a particular emphasis on the transport properties of ternary compounds and tilled compositions. The latest results obtained at JPL are presented and the possibility of obtaining high ZT values near room temperature is discussed.

Introduction

The need for more efficient thermoelectric devices has driven the study of novel semiconducting and semimetallic materials. While even modest improvements in the maximum dimensionless figure of merit ZT - currently achieved by state-of-the-art Bi_2Te_3 alloys - would be meaningful for near room temperature applications [1], thermoelectric power generators which could operate in the 200 to 1000°C temperature range are facing very stiff competition from other energy conversion technologies. This is true in particular for high power (over 200 W) automobile waste heat recovery and space applications [2,3]. For thermoelectric to be attractive, to successfully challenge competing conversion systems and to develop new wide ranging applications, ZT must attain an average value of 1.5 to 3.0, depending on the type and temperature range of the targeted application. This rationale has led to a systematic search for advanced thermoelectric materials with a good potential for maximum ZT values of 2.0 to 3.0. Studies at the Jet Propulsion Laboratory (JPL) resulted in the identification of several promising classes of materials, and in particular semiconductors with the skutterudite crystal structure [4]. Following JPL's efforts, there are now several laboratories in the United States and other countries investigating skutterudites for their thermoelectric properties. This increasing interest in skutterudites is linked to their unusual electrical and thermal transport properties which offer attractive possibilities for high ZT values. This paper will briefly review the large body of experimental data obtained to date on binary and ternary skutterudites, emphasizing common characteristics, and will attempt to provide some guidelines for optimizing thermoelectric properties near room temperature.

Crystal Structure, Existence and Composition

The prototype of the cubic skutterudite crystal structure (space group Im3) is the $CoAs_3$ compound [5], The unit cell contains square radicals of the pnicogen atoms, $[As_4]^{4-}$. This anion, located in the center of the smaller cube, is surrounded by 8 trivalent transition metal Co^{3+} cations. The unit cell consists of 8 smaller cubes, or octants, described above but two of them do not have the $[As_4]^{4-}$ anions in the center. This is necessary to keep the ratio $Co^{3+}:[As_4]^{4-} = 4:3$. Thus, a typical coordination structure results with $Co_8[As_4]_6 = 2\,Co_4[As_4]_3$ composition and 32 atoms per cell, as depicted in Figure 1. Taking into account one-half of the unit cell and its empty octant, one can represent the skutterudite formula as $\square T_4Pn_{12}$, where $\square$ is the empty octant, T is the transition metal and Pn is the pnicogen atom. If considering a simple bonding scheme [6], each transition metal contributes 9 electrons and each pnicogen contributes 3 electrons to the covalent bonding, for a valence electron count (VEC) total of 72 for each $\square T_4Pn_{12}$ unit. The VEC is a useful number in determining semiconducting skutterudite compositions. A tilled skutterudite structure is simply derived from the skutterudite structure by inserting one atom in the empty octants, as illustrated in Figure 1.

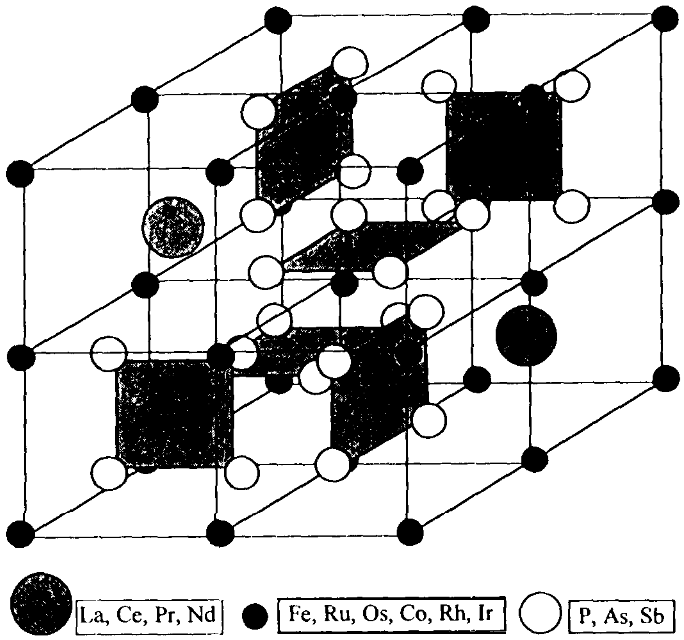

Figure 1: Skutterudite crystal structure: 32 atoms, a cubic frame with 8 transition metals, 24 pnicogens distributed in six square radicals and located in only six of the eight octants. Two rare earth elements located in the two remaining octants form a completely filled structure.

Binary compounds

Table 1. Lattice parameter a, decomposition temperature T_m, band gap Eg, of binary skutterudite compounds

Compound	a (Å)	T_m (°C)	E_g (eV)	reference
CoP_3	7.7073	>1000	0.43*	7
$CoAs_3$	8.2043	960	0.69*	8
$CoSb_3$	9.0385	850	0.63”	9
RhP_3	7.9951	>1200”	-	10
$RhAs_3$	8.4427	>1000	>0.85*	8
$RhSb_3$	9.2322	900	0.80*	9
IrP_3	8.0151	>1200	-	6
$IrAs_3$	8.4673	>1200	-	11
$IrSb_3$	9.2533	1141*	1.18*	4
NiP_3	7.8190	>850	metallic	12
PdP_3	7.705	>650	metallic	13

* JPL findings

There are eleven $\square T_4Pn_{12}$ binary skutterudites reported in the literature (see Table 1). The nine semiconducting compositions are formed with all nine possible combinations of T = Co, Rh, Ir and Pn = P, As, Sb. The existence of two more skutterudite phosphides was determined: NiP_3 and PdP_3. However, in these two compounds, the total VEC is 73, resulting in metallic behavior [15].

Known values for the lattice parameter, peritectic decomposition temperature and band gap of these nine binary compounds are reported in Table 1. Decomposition temperatures for CoP_3, RhP_3, $RhAs_3$, IrP_3 and $IrAs_3$ are only lower limit estimates. We have calculated the band gap values of $IrSb_3$, $RhSb_3$, $CoSb_3$, $RhAs_3$, $CoAs_3$, and COP, from high temperature t Ian effect measurements [I 4]. The p-type $RhAs_3$ sample was still not fully intrinsic at the highest temperature of measurement, thus the value of 0.85 should only be considered a lower limit. Less heavily doped samples must be obtained to accurately determine the band gap of $RhAs_3$. The value obtained for COP, is only preliminary because the sample used for measurement contained CoP_2 inclusions. For the arsenides and antimonides, the band gap increases in sequence from the Co- to the Ir-based compounds as well as from the antimonides to the arsenides.

Ternary compounds

Table 2: Lattice parameter a, decomposition temperature T_m, band gap Eg, electronegativity difference AX of ternary skutterudite compounds

Compound	a (Å)	T_m (°C)	E_g (eV)	AX	Ref.
$CoGe_{1.5}S_{1.5}$	8.0170	-1000	-	0.49	[16]
$CoGe_{1.5}Se_{1.5}$	8.3076”	-800	1.50*	0.47	[16]
$CoGe_{1.5}Te_{1.5}$*	8.7270”	-800	-	0.37	
$CoSn_{1.5}Se_{1.5}$*	8.7259*	~800	-	0.50	
$CoSn_{1.5}Te_{1.5}$*	9.1284*	-800	>2.0*	0.40	
$RhGe_{1.5}S_{1.5}$	8.2746	> 800	-	0.49	[17]
$IrGe_{1.5}S_{1.5}$	8.297	> 800	-	0.49	[17]
$IrGe_{1.5}Se_{1.5}$	8.5778*	>800	1.38*	0.47	[17]
$IrSn_{1.5}S_{1.5}$	8.7059	> 800	-	0.52	[17]
$IrSn_{1.5}Se_{1.5}$*	8.9674*	>800	1.24*	0.50	
$IrSn_{1.5}Te_{1.5}$*	9.3320*	>800	2.56*	0.40	
$Fe_{0.5}Ni_{0.5}Sb_3$	9.0904	729 *	-0.16*	0.12	[18]
$Fe_{0.5}Pd_{0.5}Sb_3$*	9.2060”	-	-	0.12	
$Fe_{0.5}Pt_{0.5}Sb_3$*	9.1950*	-	-	0.12	
$Ru_{0.5}Ni_{0.5}Sb_3$*	9.1780*	-		0.11	
$Ru_{0.5}Pd_{0.5}Sb_3$*	9.2960”	647 *	-0.60*	0.12	[19]
$Ru_{0.5}Pt_{0.5}Sb_3$*	-			0.12	
$Fe_{0.5}Ni_{0.5}As_3$	8.2560	-	-	0.21	[20]
$FeSb_2Se$*				0.29	
$FeSb_2Te$*	9. I 120*	556*	-0.27”	0.24	
$RuSb_2Se$*	9.2570*	-	-	0.21	
$RuSb_2Te$*	9.2680*	810*	1.20*	0.16	
$OsSb_2Te$*	9.2980’	>800	-	0.15	
$PtSn_{1.2}Sb_{1.8}$	9.3900	-	-	0.18	[21]
$NiGeP_2$*	7.9040”	-	-	0.18	
$NiGeBi_2$*	9.4400	-	-	-	

*JPL findings

The existence of many ternary skutterudites has been determined. Nine ternary compounds have been reported in the literature and seventeen more have been discovered at JPL (see Table 2). Ternary skutterudite composition are derived from binary compounds by keeping a total VEC of 72. Using □ ICo,Sbll ($CoSb_3$) as an example, substituting trivalent Co (Co") by divalent Fe (Fe^{2+}) and tetravalent Pd (Pd^{4+}), results in □ lFej NilSb12 (FeO5Ni05Sb~). If instead Sb is replaced by Sn and Te, then □ $Co_4Sn_6Te_6$ ($CoSn_{1.5}Te_{1.5}$) is obtained. If substitutions occur on both transition metal and pnicogen site, then □ $Fe_4Sb_8Te_4$ ($FeSb_2Te$) is obtained. It appears likely that more ternary skutterudites will be found, in particular among phosphides and arsenides. Using Pauli's scale, the electronegativity difference was calculated for the ternary compounds reported here. $Fe_{.5}Ni_{0.5}Sb_3$ and $FeSb_2Te$ are two ternary phases derived from $CoSb_3$, and the calculated band gap values, 0.16 and 0.27 eV respectively, are much smaller than the 0.63 eV value for $CoSb_3$. Similar results are obtained for $Ru_{0.5}Pd_{0.5}Sb_3$ (0.6 eV), which is derived from $RhSb_3$ (0.8 eV). The lower band gap values are consistent with the lower decomposition temperatures. This is not the case of $RuSb_2Te$ however, which has a band gap of 1.20 eV. As seen in Table2, it is interesting to note that the larger band gap values are indeed found in the most ionic compositions, corresponding to substitution on the pnicogen site. In addition, the lattice parameter of the ternary compounds is consistently larger than the one obtained for their binary analog. On average, the lattice parameter increases by 0.7°/0, 1.1 % and 0.6°A when substitutions respectively occur on the transition metal site, the pnicogen site , or both sites simultaneously.

Filled compounds

A large number of these compounds have been known for some time (see for example [15, 22-25]), where the tilling atom is typically a rare earth lanthanoid, though other compositions with actinoids Th and U, [22, 26] as well as alkaline earths Ca, Sr and Ba [25,27] have also been reported. For a typical filled skutterudite composition such as $LaFe_4P_{12}$, the rare earth element contributes 3 electrons, but due to the divalent Fe (Fe^{2+}), the total VEC is only 71. This deficit results in metallic behavior for most simple tilled ternary compounds. Only $CeFe_4P_{12}$, UFe_4P_{12} and $CeFe_4As_{12}$ have been reported as semiconductors, a result attributed to the higher electronegativity of phosphorus in particular which is favorable to tetravalent Ce (Ce^{4+}) instead of trivalent Ce (Ce^{3+}). However, it must be noted that Ce was found to be of intermediate valence in $CeFe_4P_{12}$. Compounds based on Th ($ThFe_4P_{12}$ has been reported) should also been semiconducting since Th is exclusively tetravalent. More recent results on filled skutterudite antimonides [28-30] based on $LaFe_4Sb_{12}$ and $CeFe_4Sb_{12}$ have shown that Fe can be replaced by Co, leading to a more semiconducting behavior in these materials. However, it was found that as Co substitution increases, the number of filling La or Ce atoms simultaneously decreases. It thus appears then that the VEC of tilled skutterudites can vary from 7 I to 72, depending on the valency of the filling atom.

Solid solutions.

The only solid solutions between binary skutterudite compounds previously reported in the literature show that CoP_3 and $CoAs_3$ form a complete range of solid solutions which obey the Vegard's rule and that the system $CoAs_{3-x}Sb_x$ has a miscibility gap in the region of x = 0.4 to 2.8 [31]. More recent experimental work at JPL has shown that there is a large number of skutterudite binary and ternary compounds, including filled skutterudites, which form solid solutions, at least in some limited range of composition [32,33].

Table 3. Existence of skutterudite solid solutions

Compound	Partial Range	Full Range
COP,		$CoAs_3$*
CoAs,	$CoSb_3$* , $IrAs_3$	
$CoSb_3$	$CoAs_3$* , $Fe_{.5}Ni_{0.5}Sb_3$, $FeSb_2Te$	$IrSb_3$, $CeFe_4Sb_{12}$
$RhSb_3$	$CoSb_3$	$IrSb_3$
$IrAs_3$	CoAs, , $IrSb_3$	
$IrSb_3$	$CoSb_3$, $IrAs_3$	$RhSb_3$, $RuSb_2Te$
$Fe_{0.5}Ni_{0.5}Sb_3$	$CoSb_3$, $IrSb_3$, $Ru_{0.5}Pd_{0.5}Sb_3$	$Ru_{0.5}Pd_{0.5}Sb_3$
$Ru_{0.5}Pd_{0.5}Sb_3$	$CoSb_3$, $IrSb_3$	$Fe_{.5}Ni_{0.5}Sb_3$
$FeSb_2Te$	$CoSb_3$, $RuSb_2Te$	
$RuSb_2Te$	$FeSb_2Te$	$IrSb_3$
$CeFe_4Sb_{12}$	$CeRu_4Sb_{12}$	$CoSb_3$

*literature results

Thermoelectric Properties of Binary Compounds

Electrical properties

The antimonides $CoSb_3$, $RhSb_3$, $IrSb_3$, and arsenides $CoAs_3$, $RhAs_3$ all exhibit semiconducting behavior, with band gap values ranging from 0.63 to 1.18 eV. These band gap values were calculated from the high temperature variations of the electrical resistivity and Hall coefficient [14]. Almost no data are available for the binary phosphides. Due to the exceptionally high hole nobilities, p-type skutterudites exhibit high electrical conductivity values, ranging from 2 to 5x105 $\Omega^{-1}m^{-1}$ for a hole concentration of 1×10^{19} cm"]. The room temperature mobility values of p-type skutterudites are I to 100 times higher than those for p-type Si and GaAs at similar carrier concentrations, as seen in Figure 2. $RhSb_3$ exhibits the greatest hole mobility, 8000 $cm^2V^{-1}s^{-1}$ for a carrier concentration of 2.5x 1018 cm-], which is about 70 times higher than p-type GaAs and still 5 times higher than n-type GaAs [9]. This is due to small hole effective mass values (as low as 0.07 m_0 for $RhSb_3$). Due to the preparation techniques used, skutterudite samples with carrier concentrations lower than 7.0×10^{16} cm"' could not been obtained so far [9]. The temperature dependencies of the carrier nobilities of the skutterudites also compare favorably with those of state-of-the-art semiconductors. Even at a temperature of 550°C, the hole mobility of $IrSb_3$ was observed to be 600 $cm^2V^{-1}s^{-1}$ for a carrier concentration of 6.5x 10^{18} cm"' -about 4 times the value obtained for n-type Si [34]. Acoustic phonon scattering of the charge carriers was found to be the dominant mechanism near room temperature for undoped skutterudites [35].

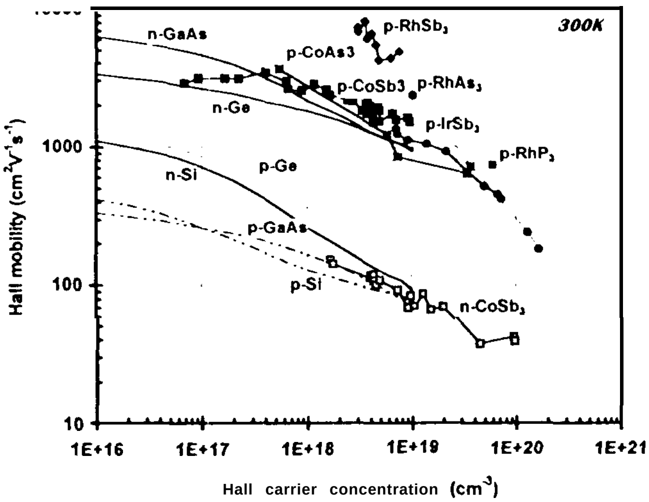

Figure 2: Room temperature Hall mobility values as a function of carrier concentration for several skutterudite compounds. Results are compared to those obtained for state of the art electronic p-type (solid lines) and n-type (dotted lines) semiconductors: Si, Ge and GaAs.

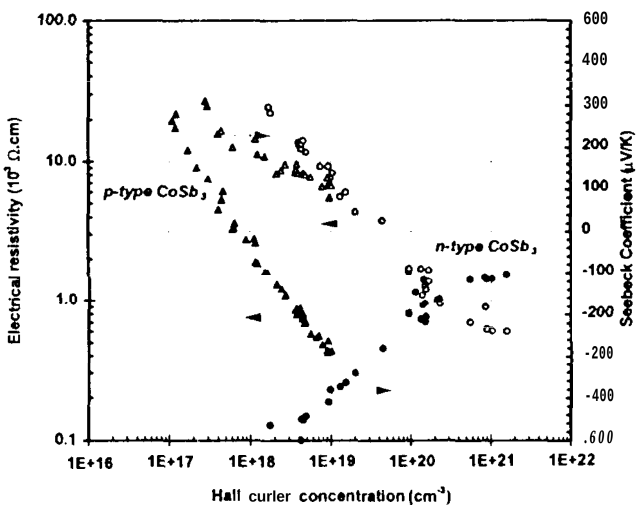

Figure 3: Room temperature electrical resist ivity and Seebeck values as a function of carrier concentration for $CoSb_3$.

Skutterudites with n-type conductivity have been obtained by doping with selected elements such as Ni, Pd, Pt and Te [34, 35]. The electron nobilities of n-type $CoSb_3$, also plotted in Figure 2, are comparable to the values obtained for p-type Si and GaAs. The calculated electron effective mass, 3. I m_0, is much larger than the hole effective mass, 0.28 m_0, in $CoSb_3$. Experimental results obtained on $CoAs_3$ and $IrSb_3$ suggest a similar behavior. It is interesting to note that these characteristics of skutterudites are the opposite of those found for Si, Ge and most II I-V compounds, where the electron effective mass is significantly smaller than the hole effective mass.

These very different characteristics lead to interesting variations of the electrical resistivity and Seebeck coefficient with carrier concentration and temperature. The room temperature variations of both transport properties are reported in Figure 3 for $CoSb_3$ as a function of the carrier concentration obtained from measurement of the Hall coefficient. It can be seen that to achieve the same electrical resistivity values n-type $CoSb_3$ samples must have carrier concentrations about fifty times higher than n-type samples. However, because of the large electron effective masses, the n-type Seebeck coefficient values are also much larger than p-type Seebeck coefficient values for the same carrier concentration,

In addition to detailed optical measurements [36], lattice dynamics studies [37,38], the electronic band structure of $CoSb_3$ has also been calculated from first principles [39]. Calculations indicated the presence of unusual features for several binary skutterudites [39,40], including the presence of a single valence band crossing the high temperature "pseudogap", resulting in an actual 50 meV gap in $CoSb_3$ and no gap in CoAs, and $IrSb_3$. In addition the gap-crossing valence band follows a linear dispersion and peculiar carrier mobility and Seebeck coefficient carrier concentration dependence were predicted. These theoretical predictions have since been completely validated by detailed experimental data [35,41].

Thermal conductivity

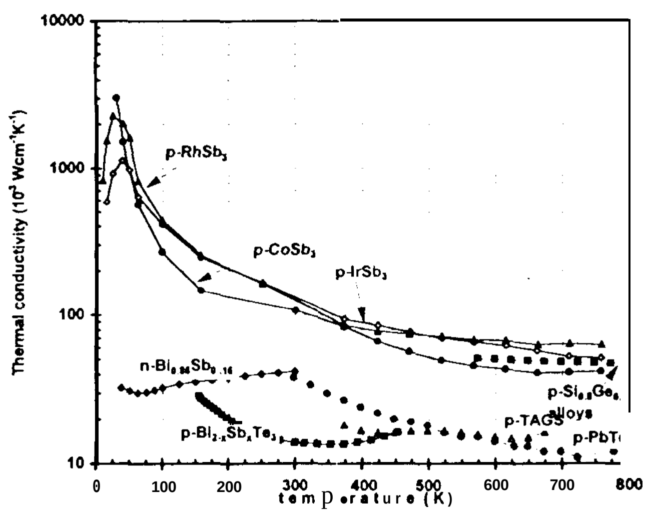

Figure 4: Thermal conductivity as a function of carrier concentration for binary skutterudite antimonides. Results are compared to those obtained for state of the art thermoelectric materials.

The thermal conductivity of lightly-doped p-type $CoSb_3$, $RhSb_3$ and $IrSb_3$ samples is plotted as a function of temperature in Figure 4. These results are similar to those obtained for CoAs, and $RhAs_3$ [8]. A simple calculation using the Wiedemann-Franz law shows that 90 to 95% of the total thermal conductivity is due to the lattice contribution near room temperature. At high temperatures, acoustic phonon scattering is mostly responsible for the decrease in thermal conductivity with a T-’ dependence [35]. Below room temperature, the very sharp rise in thermal conductivity with decreasing temperature was attributed to the dominance of the phonon-phonon umklapp scattering, and was indicative of the purity of the measured samples [41].

When compared to state-of-the-an thermoelectric materials ([0-40 m $Wcm^{-1}K^{-1}$), the thermal conductivity of binary skutterudites (100-150 m $Wcm^{-1}K^{-1}$) is too high to result in high figures of merit.

Heavily Doped n-type $CoSb_3$

As discussed in the preceding sections, both p-type and n-type $CoSb_3$ can achieve similarly attractive electrical properties, with power factor values in the 25-30 $\mu W/cmK^2$ range. However, because the optimum carrier concentration must be 50 times higher in n-type samples (- 5x10*” cm’), there are important differences in thermal conductivity and figure of merit values between p-type and n-type samples. The thermal conductivity of heavily doped n-type $CoSb_3$ samples was recently measured [35] and experimental data are shown in Figure 5. For lightly doped samples, the lattice thermal conductivity at 100”C is about 80 m $Wcm^{-1}K^{-1}$ but for more heavily doped samples, the value decreases to about 44 $mWcm^{-1}K^{-1}$ ($1x10^{20}$ cm^{-3}) and can be as low as 32 $mWcm^{-1}K^{-1}$ (IX 10^{2}’ cm^{-3}). The total thermal conductivity of the most heavily doped sample is actually higher than the one doped at 1x1020 cm^{-3} because of the large electronic contribution (proportional to the electrical conductivity).

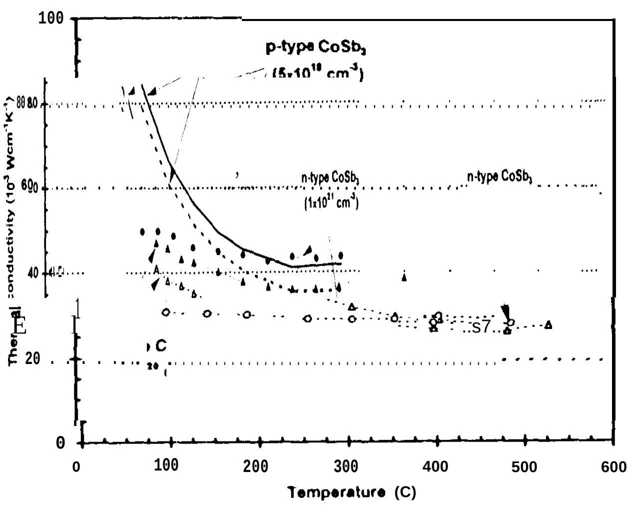

Figure 5: Lattice (dotted lines) and total (plain lines) thermal conductivity as a function of temperature for $CoSb_3$ samples with various doping levels.

The temperature dependence of the lattice thermal conductivity becomes weaker for more heavily doped samples, indicating that electron-phonon scattering is responsible for the large decrease in lattice thermal conductivity. This is an interesting finding because charge carrier phonon scattering would scatter the phonons with low frequency and if coupled with point defect scattering (by forming solid solutions) could result in very low lattice thermal conductivity values. The combination of point defects and charge carrier scattering was utilized in Si-Ge alloys [42]. Because of lower carrier concentrations, this scattering mechanism has not been identified yet in p-type samples, For optimum carrier concentrations, maximum ZT values in very heavily doped n-type $CoSb_3$ samples can reach 0.9 to 1.0 in the 550-600°C temperature range.

Ternary Compounds

Only limited information is available in the literature about the electrical and thermal properties of ternary skutterudite compounds. Some results obtained at JPL on six ternary skutterudites, $FeSb_2Te$, $RuSb_2Te$, $OsSb_2Te$, $Fe_{.5}Ni_{0.5}Sb_3$, $Ru_{0.5}Pd_{0.5}Sb_3$, $IrSn_{1.5}Se_{1.5}$ and $IrSn_{1.5}Te_{1.5}$ are reported in Figures 6, 7 and 8. $FeSb_2Te$, $Fe_{0.5}Ni_{0.5}Sb_3$ and $Ru_{0.5}Pd_{0.5}Sb_3$ appear to be heavily doped semiconductors with carrier concentrations values ranging from 1 xl O*” to lx 10^{21} cm”[3]. However, $Ru_{0.5}Pd_{0.5}Sb_3$ samples showed good carrier mobility values (about 40 cm^2/Vs near room temperature), and the a hole effective mass of 0.28mo was calculated [19]. $Fe_{.5}Ni_{0.5}Sb_3$ and $Ru_{0.5}Pd_{0.5}Sb_3$ also have low Seebeck coefficient values and mixed conduction effects are apparent in $Fe_{.5}Ni_{0.5}Sb_3$ (n-type Seebeck, p-type mobility). Relatively high Seebeck coefficients are obtained for semimetallic p-type $FeSb_2Te$ at elevated temperature, which is surprising considering the very high carrier concentration and small bandgap.

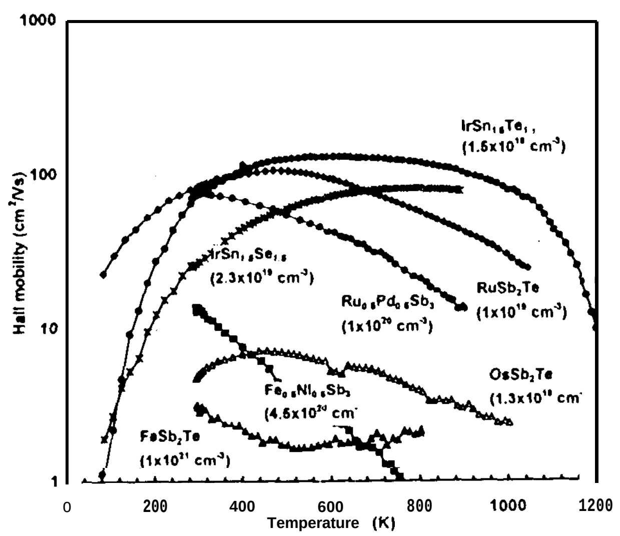

Figure 6: Hall carrier mobility as a function of temperature for several ternary skutterudite compounds. Carrier concentration levels are also reported.

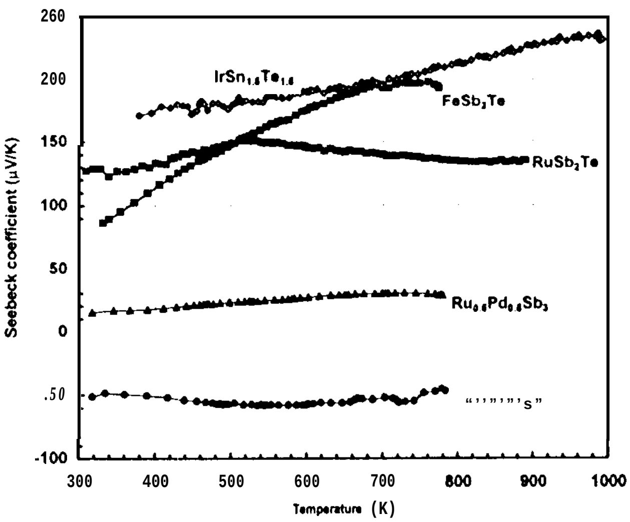

Figure 7: Seebeck coefficient as a function of temperature for several ternary skutterudite compounds.

$RuSb_2Te$, $IrSn_{1.5}Se_{1.5}$ and $IrSn_{1.5}Te_{1.5}$, have semiconducting behavior with typical carrier concentrations of 1x 10^{19} cm^{-3}, carrier mobility ranging from 50 to 100 $cm^2V^{-1}s^{-1}$ and Seebeck coefficient ranging from 120 up to 250 μVK^{-1}. All three compounds were also found to have relatively large bandgap values (over 1.2 eV). It is interesting to note that these latter materials only have one type of transition metal. Dopants, such as Ni and Te, were found to be quite ineffective in changing the carrier concentration of $FeSb_2Te$, $RuSb_2Te$ and $Ru_{0.5}Pd_{0.5}Sb_3$. From these initial experimental data, it is clear however that significant departures from the band structure and doping behavior of binary skutterudites exist in ternary skutterudites. This is confirmed in the next section when we analyze results from thermal conductivity measurements.

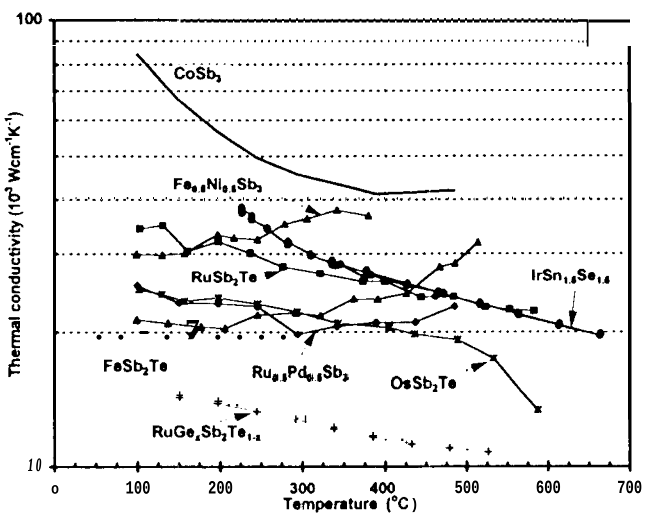

Figure 8: Thermal conductivity as a function of temperature for several ternary skutterudite compounds. Results are compared to those obtained for lightly doped $CoSb_3$.

The experimental data on the high temperature thermal conductivity of six ternary compounds, $FeSb_2Te$, $RuSb_2Te$, $OsSb_2Te$, $Fe_{0.5}Ni_{0.5}Sb_3$, $Ru_{0.5}Pd_{0.5}Sb_3$ and $IrSn_{1.5}Se_{1.5}$ and one quaternary phase, $RuGe_{0.2}Sb_2Te_{0.8}$ are plotted in Figure 8 [19, 43]. The results are compared to the data on lightly doped p-type $CoSb_3$. The lattice contribution to the thermal conductivity is greatly reduced in these materials, with room temperature values ranging from 15 to 30 $mW.cm^{-1}K^{-1}$. The low thermal conductivity values of these compounds, while very encouraging, are nevertheless a bit surprising considering that the atomic mass and volume differences introduced by the substituting anion/cation are fairly small. This indicates that additional mechanisms must be involved.

A possible explanation for the unusually high phonon scattering rate could be that transition metal elements have mixed valence states and electrons are transferred between the different ions, thus scattering the phonons in this process [43, 44]. When substituting trivalent Co (Co^{3+}) in $CoSb_3$ by Ru and Pd to form the stoichiometric $Ru_{0.5}Pd_{0.5}Sb_3$ composition, it is assumed that the valence state of Ru, and Pd, are Ru^{2+} and Pd^{4+} respectively. Systematic shifts from the stoichiometric $Ru_{0.5}Pd_{0.5}Sb_3$ were revealed by microprobe analysis [19]. Results indicate that the Ru:Pd atomic ratio can vary substantially from the expected 1:1 value and that there is a significant number of vacancies on the transition metal sublattice. To compensate for the Pd deficit and excess Sb in the samples, the Ru must adopt a mixed valence state, i.e., Ru^{2+} and Ru^{4+}. Such valence fluctuations were recently confirmed by x-ray absorption near-edge structure analysis [44].

Such stoichiometric shifts are also found for the other ternary skutterudites and experimental data for samples prepared at JPL are presented in Table 3. Based on electron microprobe analysis, each composition can be recalculated to conform to the $T^{3+}X_3^{-1}$ stoichiometry, adding vacancies to the metal sublattice when needed. The valence ratio v of the mixed valence transition metal (for example $[Ru^{2+}]/[Ru^{4+}]$) was then determined from the ionic formula. The lattice thermal conductivity calculated from the measured thermal conductivity at room temperature using the Wiedemann-Franz law is also reported in this table.

Table 1: Valence Fluctuations in Low Thermal Conductivity Ternary Skutterudites, where v is the valence ratio (e.g. $[Ru^{2+}]/[Ru^{4+}]$) and λ_L is the lattice thermal conductivity in 10^{-3} W/cmK.

Composition (at%)	Ionic Formula	v	λ_L
$Fe_{12.8}Ni_{11.9}Sb_{75.2}$	$Fe^{2+}_{0.51}Ni^{4+}_{0.49}Sb^{-1}_{3}$	--	29
$Ru_{12.3}Pd_{10.6}Sb_{77.1}$	$[]_{0.11}Ru^{2+}_{0.28}Ru^{4+}_{0.20}Pd^{4+}_{0.41}Sb^{-1}_{3}$	1.4	15
$Fe_{25.1}Sb_{52.0}Te_{22.9}$	$Fe^{2+}_{0.91}Fe^{3+}_{0.09}Sb^{-1}_{2.1}Te^{0}_{0.9}$	10.4	23
$Ru_{22.4}Sb_{49.7}Te_{25.3}$	$[]_{0.10}Ru^{2+}_{0.79}Ru^{4+}_{0.11}Sb^{-1}_{1.98}Te^{0}_{1.02}$	7.2	28
$Os_{24.6}Sb_{50.5}Te_{24.9}$	$[]_{0.02}Os^{2+}_{0.98}Os^{4+}_{0.02}Sb^{-1}_{2.03}Te^{0}_{0.97}$	32.3	25
$Ru_{24.0}Ge_{4.7}Sb_{50.6}Te_{20.7}$	$[]_{0.05}Ru^{2+}_{0.75}Ru^{4+}_{0.2}Ge^{-2}_{0.18}Sb^{-1}_{2.0}Te^{0}_{0.82}$	3.7	14
$Ir_{23.3}Sn_{38.3}Te_{38.4}$	$[]_{0.07}Ir^{3+}_{0.65}Ir^{4+}_{0.28}Sn^{-2}_{1.5}Te^{0}_{1.5}$	2.3	42

Although ternary compounds have rather low thermal conductivity values, it is difficult to control their electrical properties. When doping ternary skutterudites, and supposing that the electron exchange mechanism is indeed present, changes in carrier concentration are not easy to achieve because dopants can be compensated by small fluctuations in the overall valence of the transition metals.

Filled Skutterudites

Fe-based compositions

Recent studies have focused on Fe-based filled skutterudites, investigating the electronic band structure of $CeFe_4P_{12}$ and $CeFe_4Sb_{12}$ [45] and the transport properties of $LaFe_{4-x}Co_xSb_{12}$ and $CeFe_{4-x}Co_xSb_{12}$ compositions [28-30]. These materials are particularly attractive because of the possibility of dramatic reductions in the lattice thermal conduct ivity due to the "rattling" of the filling atorn in the two empty octants present in the skutterudite structure [46]. As briefly discussed in a preceding section, the VEC in filled skutterudites such as $LaFe_4Sb_{12}$ is only 71, resulting in metallic behavior. **This is because La only brings three electrons (La is exclusively trivalent) to compensate for the** four electron deficit due to the presence of Fe (instead of say, Co). It also has been demonstrated that Ce is nearly trivalent at temperatures higher than 100K [30]. The study of the $CeFe_{4-x}Co_xSb_{12}$ compositions was thus driven by the expectation of returning to a semiconducting $CoSb_3$-like behavior. The high temperature electrical and thermal transport properties of the $CeFe_{4-x}Co_xSb_{12}$ filled skutterudite samples have been measured from 25 up to 650°C. The temperature dependence of the electrical resistivity, Seebeck coefficient and thermal conductivity are reported in Figures 9, 10 and 11, respectively.

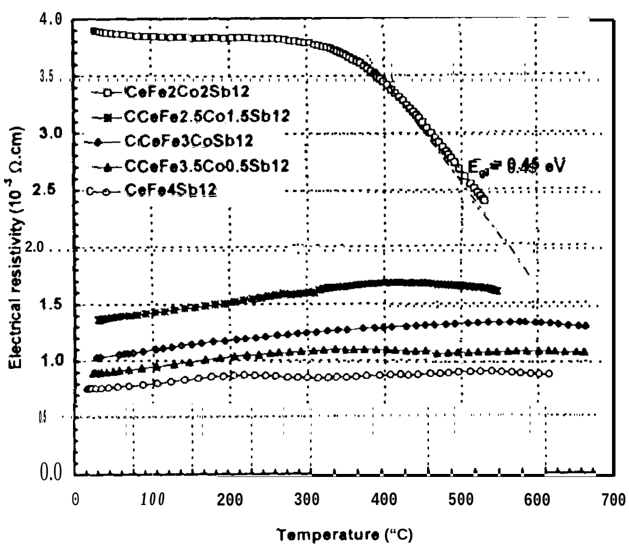

Figure 9: High temperature variations of the electrical resist ivity of p-type $CeFe_{4-x}Co_xSb_{12}$ filled skutterudites.

The results show that the Fe-rich compositions have a semimetallic behavior (very high carrier concentration of about 5x $10^{21}cm^{-3}$ and low carrier nobilities of 2-5 $cm^2V^{-1}s^{-1}$) with a low electrical resistivity, which increases slightly with temperature. However, the $CeFe_2Co_2Sb_{12}$ sample demonstrated a more semiconducting behavior, with a bandgap value of 0.45 eV determined from high temperature electrical resistivity measurements

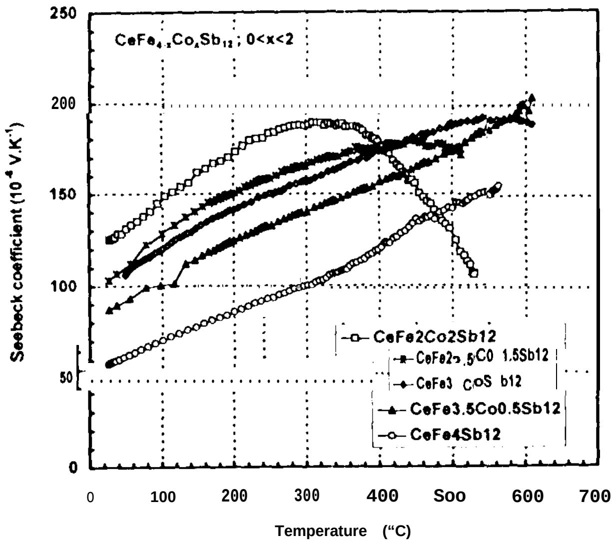

Figure 10: High temperature variations of the Seebeck coefficient of p-type $CeFe_{4-x}Co_xSb_{12}$ filled skutterudites.

What is most surprising is the magnitude of the Seebeck coefficients, ranging from 55 to 125 μVK^{-1} at 25°C and increasing steadily with temperature. Again, the intrinsic regime is obtained in $CeFe_2Co_2Sb_{12}$ **for temperatures over** 350°C. These values are comparable to those obtained for other p-type binary skutterudites except that here the *carrier* concentration is two to three orders of magnitude higher. This is attributed to the fact that these materials behave similarly to heavy fermions systems: the hybridization between Ce and the transition metal (Fe or Co here) creates a small bandgap and carriers possess large effective masses resulting in a low mobility but unusually high Seebeck coefficient [45,47].

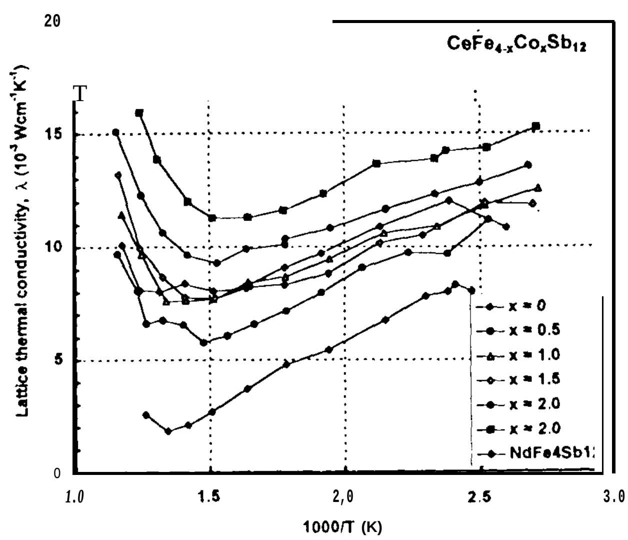

Figure 1 I: Lattice thermal conductivity as a function of inverse temperature for $CeFe_{4-x}Co_xSb_{12}$ filled skutterudites.

As shown in Figure I 1, the lattice thermal conductivity of tilled skutterudites is much lower than the values obtained for $CoSb_3$. The $CeFe_4Sb_{12}$ sample has a room temperature thermal conductivity of about 24 $x10^{-3}$ $Wcm^{-1}K^{-1}$ at room temperature and increasing up to 27 xl $0^{-3}Wcm^{-1}K^{-1}$ at 575°C. Based on the low electrical resistivity value (0.5x $10^{-3}\Omega cm$), the lattice contribution to the thermal conductivity was estimated at 12 $x10^{-3}Wcm^{-1}K^{-1}$ This demonstrates that the combination of the "rattling" atom and very high carrier concentration (5x 10^{21} cm-') very effectively scatter the phonons, and results in an extremely low lattice thermal conductivity. Similar low thermal conductivity values have also been obtained on $IrSb_3$-based filled skutterudite compositions [48,49].

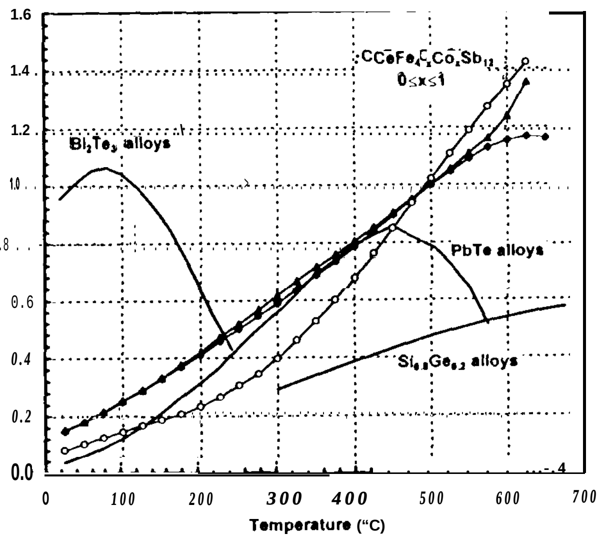

Figure 12: ZT as a function of temperature for $CeFe_{4-x}Co_xSb_{12}$ samples, with 0<x<1.0.

The combination of the low electrical resistivity, moderate Seebeck coefficient and low thermal conductivity resulted in high ZT values at temperatures above 400°C for the Fe-rich compositions (Figure 12). A maximum **ZT** value of 1.4 has been achieved to date at a temperature of 600°C [28]. High ZT values have also been reported on similar compositions filled with La instead of Ce [29]. However, because of the semimetallic behavior of the $CeFe_{4-x}Co_xSb_{12}$ compositions it is difficult to control carrier concentration, obtain n-type conductivity samples and optimize the thermoelectric properties at various temperatures. To do so requires the preparation of semiconducting filled skutterudites with good carrier mobility values.

Skutterudites for Low Temperatures

Electron microprobe analysis of a series of $CeFe_{4-x}Co_xSb_{12}$ has demonstrated that the amount of Ce tilling decreases with increasing substitution of Fe by Co. One can rewrite those compositions with the following formula, $Ce_fFe_{4-x}Co_xSb_{12}$, where f represent the fraction of Ce filling (f = 1 represents complete filling). [n addition to Co, substitution of Fe by Ni and Ru has also been investigated recently. The variations of the filling fraction f as a function of x have been plotted in Figure 13 for the three different ranges of compositions. The two solid lines represent the expected transition for Ni and Co from p-type to n-type (when the VEC reaches 72), taking into account both f and x variations. When Fe is totally replaced by Co, only a very small amount of Ce remains in the sample (f= 0.07) while completely filled $CeRu_4Sb_{12}$ can be prepared **(f= l). This is attributed to the fact that** Ru and Fe are isoelectronic. The dotted line was calculated based on a $CeFe_4Sb_{12}$-$Ce_{0.065}Co_4Sb_{12}$ range of "solid solution" compositions. $Ce_fFe_{4-x}Ni_xSb_{12}$ compositions with x >1.5 have not yet been synthesized, but it is clear that at equivalent concentrations, Ni substitution results in less Ce tilling than Co substitution. However, because Ni donates two electrons instead of only one for Co when replacing **Fe,** the decrease in carrier concentration and corresponding change in properties with increasing x is **much stronger** for $Ce_fFe_{4-x}Ni_xSb_{12}$.

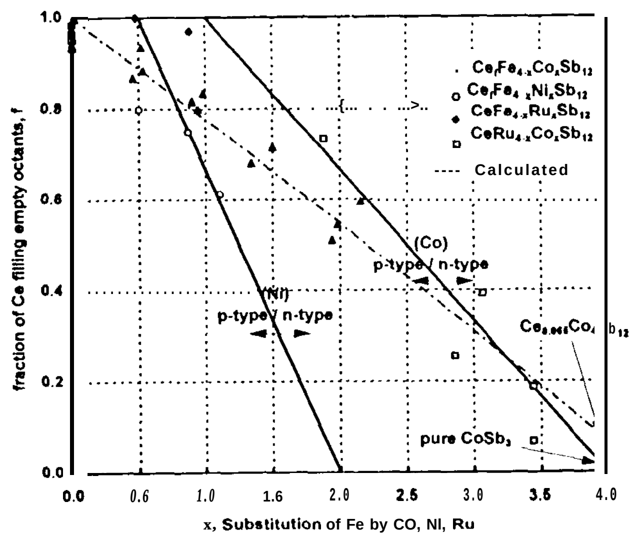

Figure 13: Ce filling fraction (f) for $Ce_fFe_{4-x}M_xSb_{12}$ samples as a function of Fe substitution by M (x) with M = Co, Ni and Ru. No decrease in Ce filling is observed for $Ce_fFe_{4-x}Ru_xSb_{12}$ samples.

While it is clear that filling the skutterudite structure contributes to the low lattice thermal conductivity, high carrier concentrations and valence fluctuations could also strongly scatter phonons in the compositions studied so far. Indeed, a typical carrier concentration value of 5x 10^{21} cm-' is obtained for $CeFe_4Sb_{12}$ at 300K, while a carrier concentration of 4x 1020 cm^{-3} was **measured for both** $Ce_{0.51}Fe_{2.1}Co_{1.9}Sb_{12}$ **and** $Ce_{0.75}Fe_{3.1}Ni_{0.9}Sb_{12}$ compositions. The Co-based sample has 51% of its voids tilled with Ce while the Ni-based sample has 75% of filled voids, but their lattice thermal conductivity is nearly identical, 16 to 17x10 $^{-3}$Wcm "K-l, to be compared with a value of 12x10 $^{-3}Wcm^{-1}K^{-1}$ for $CeFe_4Sb_{12}$.

Another interesting result is the fact that no decrease in lattice thermal conductivity was observed when Ru was substituted for Fe. It seems that the point defects generated by a Ru atom on the Fe site do not contribute any further to the overall scattering rate, possibly because void fillers already scatter phonons in a wide frequency domain. Very recent experimental data obtained at JPL on $Ce_fRu_{4-x}Co_xSb_{12}$

samples suggests another possibility. Figures 14, 15 and 16 respectively present Hall mobility, Seebeck coefficient and thermal conductivity variations with temperatures for selected Fe-based, Ru-based and Co-based filled skutterudites. The actual tilling fraction as determined from electron microprobe analysis is also reported.

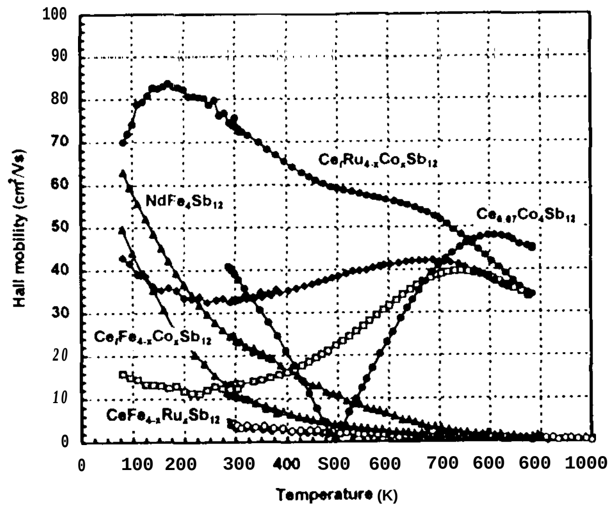

Figure 14: Hall carrier mobility as a function of temperature for various Fe-, Ru-, and Co-based filled skutterudites.

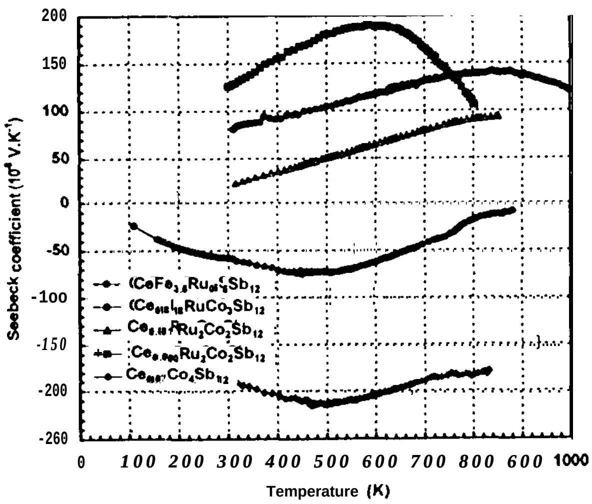

Figure 15: Seebeck coefficient as a function of temperature for various Fe-, Ku-, and Co-based filled skutterudites.

The data show that there are very significant differences between filled skutterudite compositions containing some amount of Fe and those which only have Ru and Co. Much higher p-type carrier mobility (up to 75 $cm^2V^{-1}s^{-1}$ at room temperature) are obtained for an 1 8% filled $Ce_fRuCo_3Sb_{12}$ sample. Comparable compositions with Fe have been reported to have very poor nobilities [50]. In addition n-type $Ce_fRuCo_3Sb_{12}$ and $Ce_fCo_4Sb_{12}$ samples were successfully prepared. These n-type samples show mixed conduction effects very similar to those observed in n-type $CoSb_3$ and $IrSb_3$. The tilling of just 7% of the empty octants of a semiconducting $CoSb_3$ sample resulted in a large drop in the room temperature lattice thermal conductivity, from 95 to about 35 $10^{-3}Wcm^{-1}K^{-1}$. Substitution of Co by Ru and a subsequent increase in Ce filling succeeded in further reduction in the lattice thermal conductivity, likely due to a combination of point defect and increased void filling phonon scattering.

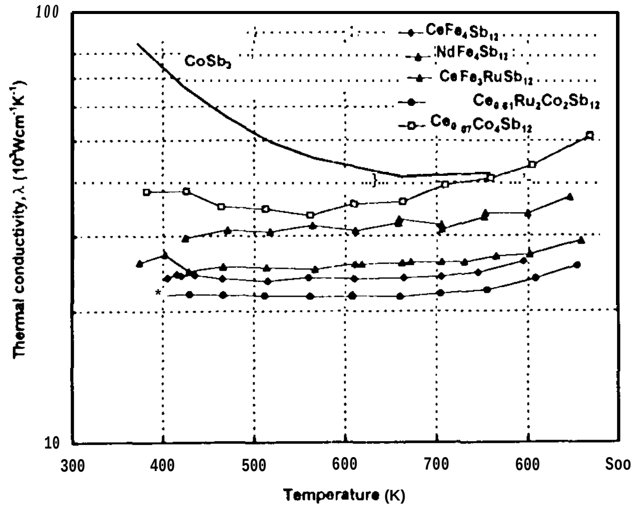

Figure 15: Thermal conductivity as a function of temperature for various Fe-, Ru-, and Co-based filled skutterudites. Results are compared to p-type $CoSb_3$ data.

However. Fe-based filled skutterudites, despite much higher carrier concentrations, consistently possess larger p-type Seebeck coefficient and lower lattice thermal conductivity. It is interesting to note that qualitatively similar remarks can be made for the $FeSb_2Te$ and $Fe_{0.5}Ni_{0.5}Sb_3$ ternary compounds compared to their Ru-based analogs, $RuSb_2Te$ and $Ru_{0.5}Pd_{0.5}Sb_3$. First principle electronic band structure calculations of Ru-based filled skutterudites would be of great interest [5 1]. Even though these new results are not fully understood, the preparation of p-type and n-type semiconducting filled skutterudites with filling fractions of up to 60% offers new possibilities for optimizing their thermoelectric properties near room temperature.

Conclusion

The properties of binary skutterudite compounds are very attractive for thermoelectric applications. However, their lattice thermal conductivity values are too high, in particular at low temperatures. Several approaches to significantly reduce the thermal conductivity of skutterudites have been identified: heavy doping, solid solution formation, valence fluctuations, and void filling. Ultimately, a combination of these approaches should be employed to reach a lattice thermal conductivity close to the theoretical minimum. Recent results have shown that high ZT values substantially larger than 1.0 can be obtained for some skutterudite solid solutions and filled compositions at temperature near 600°C. New experimental data on Ru-based semiconducting filled skutterudite compositions offer a promising approach for achieving high ZT in skutterudites at lower temperatures.

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References

1. H. Lyon, *Proceedings, Materials Research Society Spring Meeting, Symposium Q,* ed. T. Tritt, ([997).

2. A. Schock, *Proceedings, 14th [international Conference on Thermoelectrics,* ed. M. Vedemikov, Ioffe Physico-Technical Institute, p. 231 (1 995).

3 . D.T. Morelli, *Proceedings, 15th International Conference on Thermoelectric,* ed. T. Caillat (IEEE Catalog 96TH8169), p. 112 (1996).

4 . T . Caillat, A. Borshchevsky, and J.-P. Fleurial, Proceedings, 7th International Conference on Thermoelectrics, ed. K. Rae, University of Texas at Arlington, p. 98 (1993).

5. Oftedal, I., Z. Kristallogr., 66,517 (1928).

6. S. Rundqvist and N.-O. Ersson, Arkiv for Kemi, 30 **(10),** 103 (1968).

7. W. Biltz and M. Heimbrecht, Z. Anorg. Allgem. Chem. 241,349 (1939).

8. T. Caillat, J.-P. Fleurial, and A. Borshchevsky, *Proc.* 30th *Intersoc. Ener. Conv. Engin. Conf.,* Orlando, Florida, August 3-7, (199s).

9. T. Caillat, J.-P. Fleurial, and A. Borshchevsky, J. Crystal Growth, 166,722-726 (1996).

10. J. P. Odile, S. Soled, C. A. Castro, A. Weld, Inorganic Chemistry, 17,2,283 (1978).

11. A. Kjekshus and G. Pedersen, "The Crystal Structure of $IrAs_3$ and $1rSb_3$", Acts Cryst., 14, 1065-1070 (196 1).

12. S. Rundqvist and E Larsson, Acts Chem. Stand. 13, 551 (1959).

13. S. Rundqvist, Nature, 185,31 (1 960).

14. J.-P. Fleurial, T. Caillat, A. Borshchevsky, *Proc. 13th Intl. Conf. on Thermoelectric,* AIP Press No. 316, 40-44, Kansas City, MO (1994).

15. W. Jeitschko and D. Braun, Acts. Cryst., B33, 3401-3406 (1977).

16. R. Korenstein, S. Soled, A. Weld, G. Collin, Inorganic Chemistry, 16,9,2344 (1977).

17. A. Lyons, R. P. Gruska, C. Case, S. N. Subbarao, A. Weld, Mat. Res. Bul., 125 (1978).

18. A. Kjekshus, T. Rakke, Acts Chemica Scandinavia, A28, 99 (1974).

19. T. Caillat, J. Kulleck, A. Borshchevsky, and J.-P. Fleurial, J. Appl. Phys. vol. 79, 11, 1 141 (1996).

20. I 1. D. Lutz, G. Kliche, J. Solid State Chemistry, 40, 64 (1981).

21. S. Bahn, T. Gödecke, , K. Schubert, J. of Less-Common Metals, 19, 121 (1969).

22. G. P. Meisner, M. S. Torikachvili, K. N. Yang, M. B. Maple, R. P. Guertin, J. Appl. Phys., 57, 1, 3073 (1985).

23. D. Jung, M. H. Whangbo, S. Alvarez, Inorganic Chemistry, 29,2252 (1990).

24. F. Grandjean, A. Gérard, D. J. Braun, W. Jeitschko, J. Phys. Chem. Solids, 45, 8/9, 877 (1984).

25. N. T. Stetson, S. M. Kauzlarich, H. Hope, Journal of Solid State Chemistry, 91, 140 (199 1).

26. D. J. Braun and W. Jeitschko, J/ Less Common Metals, 76.33 (1980).

27. M. E. Danebrock, C. B. H. Evers and W. Jeitschko, J. Phys. Chem. Solids, 57 (4)38 I (1996).

28. J.-P. Fleurial, A. Borshchevsky, and T. Caillat, D. T. MorelIi, and G. P. Meisner, *Proceedings, 15th International Conference on Thermoelectric,* ed. T. Caillat (IEEE Catalog 96TH8169), p. 91 (1996).

29. B.C. Sales, D. Mandrus and R.K. Williams, Science, Vol. 22, 1325-1328 (1996).

30. B. Chen, J.H Xu, C. Uher, D.T. MorelIi, G.P. Meisner, J.-P. Fleurial, T. Caillat and A. Borshchevsky, Phys. Rev. B. 55 (3) 1476-1480 (1997).

31. N. Mandel, J. Donohue, Acts Cryst., B27, 2288 (1971).

32. A. Borshchevsky, J.-P. Fleurial, C.E. Allevato, and T. Caillat, , *Proc. 13th Intl. Conf. on Thermoelectric,* AIP Press No. 316, 3-6, **Kansas City, MO (1994).**

33. A. Borshchevsky, J.-P. Fleurial, and T. Caillat, *Proceedings, 15th International Conference on Thermoelectric,* ed. T. Caillat (IEEE Catalog 96TH8 169), p. 112(1996).

34. T. Caillat, A. Borshchevsky, and J.-P. Fleurial, J.-P., *Proc. 13th Intl. Conf. on Thermoelectric,* AIP Press No. 316, 31-34, Kansas City, MO (1994).

35. T. Caillat, A. Borshchevsky, and J.-P. Fleurial, J. Appl. Phys. 80 (8) 4442-4449 (1996).

36. J. Ackermann and A. Weld, J. Phys. Chem. Solids, 38, 1013 (1977).

37. G.S. Nolas, G.A. Slack, T. Caillat and G.P. Meisner, J. Appl. Phys. 79 (5) 2622-2626 (1996).

38. J.L. Feldman and D.J. Singh, Phys. Rev. B, 53 (10), 6273-6282 (1 996).

39. D.J. Singh and W.E. Pickett, Phys. Rev. B, 50 (1 1), 235 (1994).

40. M. Llunell. P. Alemany, S. Alvarez and V. P. Zhukov, Phys. Rev. B, 53 (16), 106O5-106O9 (1996).

41. D.T. MorelIi, T. Caillat, J.-P. Fleurial, A. Borshchevsky, J. Vandersande, B. Chen and C. Uher, Phys. Rev. B, 5 l (15), 9622-9628 (1995).

42, J. P. Dismukes, L. Esktröm, E. F. Steigmeier, l., Kudman, and D. S. Beers, J. Appl. Phys., vol. 35, p. 2899 (1964).

43. G. A. Slack, J.-P. Fleurial, and T. Caillat, Naval Research Reviews, Vol. XLVIII, 23-30 (1996).

44. G.S. Nolas, V.G. Harris, T.M. Tritt and G.A. Slack, J. Appl. Phys. 80(11) 6304-6308 (1996).

45. L. Nordstrom and D.J. Singh, Phys. Rev. B, 53 (3), 9622-9628 (1996).

46. G. A. Slack, Thermoelectric Handbook, ed. by M. Rowe (Chemical Rubber, Boca Raton, FL), p. 407(1995).

47. D.T. Morelli and G.P. Meisner, J. Applied Physics 77, 3777 (1995)

48. G. S. Nolas, G. A. Slack, T. M. Tritt, and D. T. MorelIi, J. Applied Physics 79 (8) 4002-4008 (1996).

49. T. M. Tritt, G. S. Nolas, G. A. Slack, A.C. Ehrlich, D.J. Gillespie and J.L. Cohn ,J. Applied Physics 79 (11) 8412-8418 (1 996).

50. D.T. MorelIi, private communication.

51. D.J. Singh, private communication.